

## 9.—THE ESSENTIAL OILS OF THE WESTERN AUSTRALIAN EUCALYPTS.

## PART II.

THE OILS OF *E. KESSELLI* AND *E. DUNDASI*,

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EUCALYPTUS KESSELLI, Maiden et Blakely.<sup>(1)</sup>

*E. Kesselli* occurs in a belt of country extending from Salmon Gums in the north to Scaddan in the south; it does not extend far to the west and its eastern limit has not been defined.

The leaves of the tree are thick, flat and coriaceous, varying somewhat in shape from straight or curved lanceolate to ovate lanceolate. They are up to 1¼ inches wide and from 3 inches to 4½ inches long and are thickly dotted with oil glands. The venation is fairly distinct and resembles closely that of *E. Flocktoniae* (see Part I.), so that the oil might be expected to consist mainly of cineol and pinene.

The material for distillation was collected by Mr. G. H. Burvill, B.Sc. (Hons.), from Fitzgerald Location 422, about 8 miles east of Circle Valley, near Salmon Gums, during the last week in July, and was identified by Mr. C. A. Gardner, Government Botanist. It was obtained from normal mature trees and when distilled was in good fresh condition.

The oil distilled slowly, probably owing to the thick nature of the leaves, and was a pale yellowish-green in colour. The yield was 1.23 per cent. by weight. Its density, refractive index, optical rotation and solubility in alcohol were all very similar to those of *E. Flocktoniae*. The oil contained a little more free acid than that of *E. Flocktoniae* and its ester content (indicated by its saponification value) was also somewhat greater; the proportion of alcohols, however, although still very great, was somewhat less than in *E. Flocktoniae*. The amount of pinene in the two oils is much about the same but there is a little less cineol in the oil of *E. Kesselli*; on the other hand, the rectified oil (boiling below 195° C.) contains somewhat more cineol (64 per cent.) than the rectified oil of *E. Flocktoniae* (61.5 per cent.), but even so this is not sufficient for a medicinal oil. Aldehydes are absent but an intense yellow colour with ferric chloride suggests the presence of phenolic substances. The sesquiterpene aromadendrene is present in fair quantity and no indication was obtained of the presence of phellandrene.

The same separation of white insoluble substance, mentioned in connection with the oil of *E. Flocktoniae* (Part I., page 103), was noted in the fractional distillation of this oil. It was recovered from the residue as before and found to make up 3.45 per cent. of the original oil.

*E. Kesselli* therefore belongs to the main group of Western Australian eucalypts, possessing an oil of the predominating cineol-pinene type, without containing any aromadendral or phellandrene.

(1) Maiden and Blakely: Jour. Roy. Soc., N.S.W., Vol. 59, 1925, p. 187.

EUCALYPTUS DUNDASI, Maiden.<sup>(2)</sup>

*E. dundasi*, known as Dundas blackbutt, is described by Kessell and Gardner.<sup>(3)</sup> The leaves are fairly leathery and thick, up to  $\frac{1}{2}$  inch or a little more in width and from 3 to 5 inches in length. The midrib is prominent and the veins roughly parallel and generally similar to those already described in this series (*E. Flocktoniae* and *E. Kesselli*); the submarginal vein is close to the edge of the leaf but shows the characteristic incurving common to leaves which contain cineol as a main constituent of their oil. The leaves only show minute oil glands.

The material used was collected about the middle of August, 1934, on Fitzgerald Location 930, about 2 miles west of Kumarl, near Salmon Gums, by Mr. G. H. Burvill, and it was identified by Mr. C. A. Gardner. It was obtained from vigorously growing young trees and saplings, from 10 to 20 feet in height.

The leaves were slightly mouldy near the young tips when distilled, but were otherwise in good condition. The oil distilled fairly quickly, but the yield was low, only 18 grams being obtained from 9 kilograms of material. It was pale yellow in colour and had a pleasant odour. Its density and refractive index were lower than those of *E. Flocktoniae* and *E. Kesselli* and its solubility in alcohol also less, suggesting that it contained a higher proportion of terpene, probably pinene. That the pinene present was *d*-pinene was indicated by the fairly high dextrorotation ( $+10.65^\circ$ ) of the oil. The acid value was low but the ester value was comparatively high; sufficient oil was not available to determine the acetyl value. The cineol content was 32 per cent. which would correspond to about 45 per cent. in the rectified oil. The oil gave no pronounced reaction with ferric chloride and gave no test with Schiff's reagent, showing the absence of aromadendral. The presence of aromadendrene in quantity was indicated by strong positive tests being obtained with the usual reagents.

Fractionation showed that the oil contained a high proportion of pinene, nearly 15 per cent. being volatile below  $162^\circ\text{C}$ .; 71 per cent. of the oil was volatile below  $195^\circ\text{C}$ . and from the residue the usual white insoluble material was isolated in 1.3 per cent. yield. No evidence was obtained to suggest the presence of phellandrene.

The oil of *E. dundasi* is therefore of the same type as those of *E. Flocktoniae* and *E. Kesselli*, but the smaller amount of cineol, together with the larger amount of pinene, suggest that the tree is a more primitive species. The oil is, of course, owing to its poor yield, of no commercial interest.

## EXPERIMENTAL.

## EUCALYPTUS KESSELLI.

The oil was distilled from the leaves within three weeks of collection, the leaves in the centres of the bags being appreciably warm from fermentive changes which had occurred. It distilled very slowly, taking some six hours to complete; 53 mls of the oil were obtained from 4 kilograms of material,

(2) Maiden: Proc. Roy. Soc., N.S.W., Vol. 49, 1915, p. 309.

(3) Kessell and Gardner: A Key to the Eucalypts of Western Australia.

representing a yield of 1.23 per cent. by weight. The oil was a pale yellowish green in colour and had a fairly pleasant odour; after drying over anhydrous sodium sulphate, it had the following properties:—

Specific Gravity*	..	..	..	..	..	0.9248
Refractive Index	..	..	..	..	..	1.4728
Optical Rotation	..	..	..	..	..	Nil
Acid Value	..	..	..	..	..	3.38
Saponification Value	..	..	..	..	..	9.4
Acetyl Value	..	..	..	..	..	79.4

The oil was soluble in 2 volumes of 70 per cent. (by weight) alcohol.

The saponification value corresponds to 3.3 per cent. of esters calculated as geranyl acetate, whilst the acetyl value corresponds to 19.2 per cent. of alcohols calculated as geraniol. The cineol content, determined by the melting point method with *o*-cresol, was 44.2 per cent.

No reaction was obtained with Schiff's reagent, showing the absence of aldehydes. An intense yellow colour was given by an alcoholic solution of the oil when tested with neutral ferric chloride, indicating the presence of phenols. A solution of the oil in glacial acetic acid gave all the usual colour reactions for aromadendrene (see Part I., p. 104).

#### FRACTIONATION.

100 grams of the oil were fractionally distilled at atmospheric pressure. As the liquid commenced to boil, it gradually became cloudy and finally quite opaque owing to the separation of the white insoluble substance already referred to (Part I., p. 103). The following fractions were obtained:—

1. Up to 140°C.	..	..	..	..	1.45 per cent.
2. From 140°—170°C.	..	..	..	27.7	„ „
3. From 170°—180°C.	..	..	..	27.6	„ „
4. From 180°—195°C.	..	..	..	14.9	„ „
Residue	..	..	..	28.35	„ „

The rectified oil distilling between 140° and 195°C. made up 70.2 per cent. of the original oil and contained 64 per cent. of cineol, corresponding to 44.9 per cent. in the original oil.

Fraction 1 was pale yellow in colour and contained a small amount of water. It gave no colouration with ferric chloride and no reaction with Schiff's reagent. Its refractive index was 1.4644; there was not sufficient oil to measure the density or optical rotation.

Fraction 2 was pale greenish yellow in colour and had the following physical properties:—Specific gravity, 0.8915; refractive index, 1.4632; optical rotation, +19.35°. It gave no reactions for phenols or aldehydes. Refractionation of the combined fractions 1 and 2 finally gave a colourless distillate, amounting to 5.4 per cent. of the original oil, distilling between 156° and 158° C.; from this fraction, pinene nitrosochloride (m.p. 104° C.) was isolable in quantity. The dextrorotation of the fraction indicates that this is present as *d*-pinene.

\* All physical properties are given at 20° C. unless otherwise stated.

Fraction 3 was similar in colour to fraction 2; it had the following properties:—Specific gravity, 0.9103; refractive index, 1.4646; optical rotation,  $+5.25^\circ$ . No reactions were obtained for the presence of phenols or aldehydes.

Fraction 4 was practically colourless and had the following properties:—Specific gravity, 0.9346; refractive index, 1.4704; optical rotation,  $-11.35^\circ$ . It also gave no reactions for phenols or aldehydes.

The residue was taken up in ether, so precipitating the white insoluble compound which was filtered off, washed with a little ether, dried and weighed; the yield was 3.45 per cent. From the combined ether filtrates, the ether was removed and the residue (24.5 grams) tested for phenols, aldehydes and aromadendrene. It gave all the colour reactions for aromadendrene, gave a strong yellow colour with ferric chloride, but gave no reactions for aldehydes; aromadendral was therefore absent.

On fractionation, the residue gave 12.9 grams distilling between  $96^\circ$  and  $140^\circ$  C. at 23 mms. as a pale yellow viscous oil, of refractive index 1.4924, and 8.4 grams distilling between  $140^\circ$  and  $163^\circ$  C. at 23 mms. The second fraction was very viscous and a deep golden yellow in colour and had a refractive index 1.5020.

#### EUCALYPTUS DUNDASI.

The oil obtained by steam distillation of the leaves and terminal branchlets had, after drying over sodium sulphate, the following properties:—

Specific gravity	..	..	..	..	0.9075
Refractive index	..	..	..	..	1.4694
Optical rotation	..	..	..	..	$+10.65^\circ$
Acid value	..	..	..	..	1.07
Saponification value	..	..	..	..	38.4

It was pale yellow in colour and was soluble in an equal volume of 80 per cent. alcohol. Its saponification value corresponds to 13.4 per cent. by weight of esters calculated as geranyl acetate. There was not sufficient oil available to determine the acetyl value. The oil contained 32 per cent. of cineol determined by the *o*-cresol method. It gave very little colour with ferric chloride and gave no reactions for aromadendral; strong positive reactions were obtained for aromadendrene.

#### FRACTIONATION.

11.3 grams of the oil were distilled at ordinary pressure and the following fractions obtained:—

1. Up to $162^\circ$ C.	..	..	..	14.7 per cent.
2. From $162^\circ$ - $170^\circ$ C.	..	..	..	32.4 " "
3. From $170^\circ$ - $182^\circ$ C.	..	..	..	17.4 " "
4. From $182^\circ$ - $195^\circ$ C.	..	..	..	6.3 " "
5. From $195^\circ$ - $230^\circ$ C.	..	..	..	9.8 " "
Residue	..	..	..	18.6 " "

As the oil commenced to boil, the separation of white insoluble matter was again noted; this had almost completely redissolved by the time the distillation was stopped.

Fraction 1 was colourless and had a strong pinene odour. Its refractive index was 1.4619, but there was not sufficient to measure the density or optical rotation.

Fractions 2 and 3 were very similar to one another, both being colourless and having refractive indices of 1.4601 and 1.4606 respectively. They gave no reactions for phenols or aldehydes.

Fraction 4 had a very faint yellow colour and its refractive index was 1.4642. With the preceding fraction it made up 70.8 per cent. of the original oil, a figure very close to the corresponding fractions of *E. Flocktoniae* and *E. Kesselli*.

Fraction 5 was pale yellow in colour, had refractive index 1.4752, and gave all the characteristic reactions for aromadendrene. It gave no reactions for aldehydes or phenols.

The residue (2.1 grams, representing 18.6 per cent. of the original oil) was taken up in ether and the white insoluble material filtered off and washed with ether. The amount recovered corresponded to 1.3 per cent. of the oil. After removal of the ether from the filtrate, the residue gave all the tests for aromadendrene, gave a slight colouration with alcoholic ferric chloride, but gave no reaction with Schiff's reagent.

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